Synthesis and Liquid Crystalline Properties of Novel Imides and Thioimides with Chiral Aliphatic Tails

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Three chiral compounds (*R*)-octan-2-ol, (*S*)-citronellol and (*S*)-citronellyl bromide were used for the synthesis of novel ester imides with biphenyl moieties as mesogenic units. Observations by means of polarising microscopy as well as DSC measurements revealed the presence of SmC* and/or SmA phases for all the compounds examined. It was found that the biphenyl units with long chiral alkoxy substituents induce smectic C phases.

Key words: Imides, Thioimides, Liquid Crystals

Introduction

Systematic studies by Kricheldorf's group have proved that aromatic imide moieties are relatively poor mesogens despite their planarity, rigidity and polarity [1 – 4]. Surprisingly, the symmetrical imide units which were expected to be rather good mesogens proved to be almost non-mesogenic. Another tendency is observed for ester groups. They highly favour the formation of liquid crystalline phases. It should be noticed that these findings were made for high molecular compounds such as polyimides and poly(ester imides). However, low molecular liquid crystalline ester imides were studied mainly by our team [5 – 10]. In our previous publication we described the synthesis of a series of imides and thioimides with chiral *N*-substituents derived from (*S*)-2-methylbutan-1-ol as well as (*S*)-2-aminobutane [6]. Liquid crystalline smectic phases occurred in all the compounds studied. The general formula is recalled in Fig. 1.

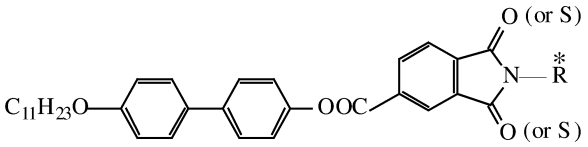
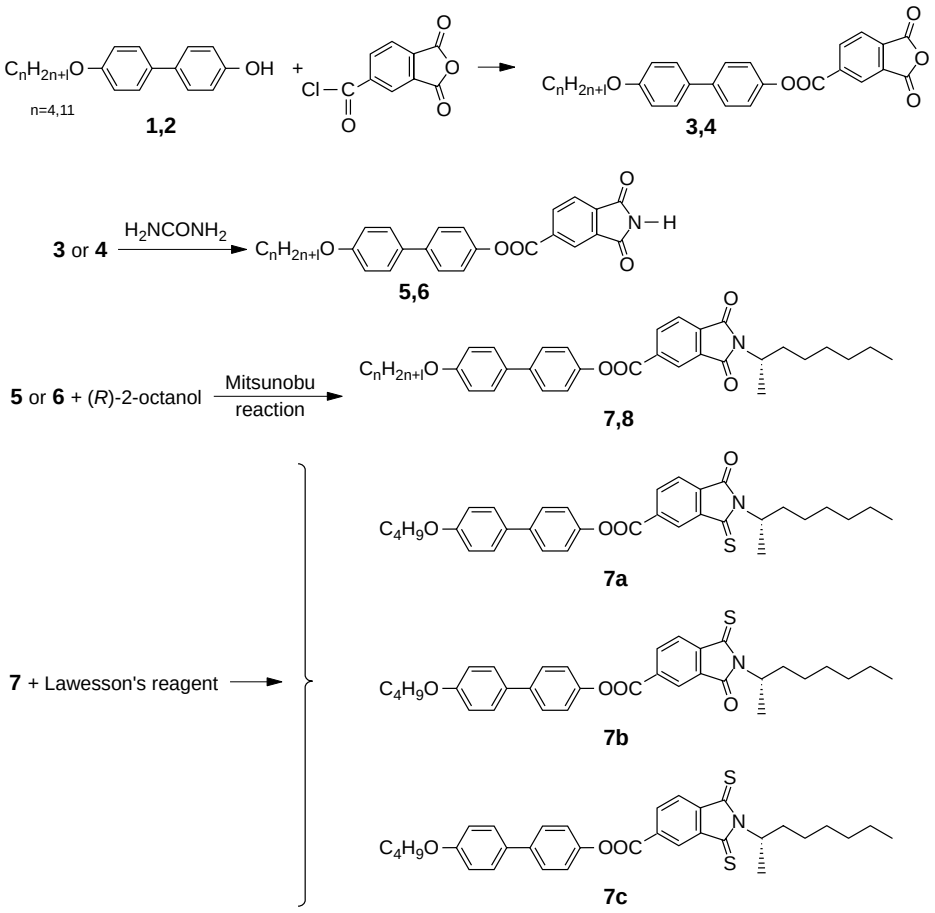


Fig. 1. General structure of liquid crystalline imides and thioimides

The presence of chiral centres in molecules may induce various smectic phases, for example N*, SmA*, SmC*, SmC^*_F [6 – 10]. A wide variety of liquid crystalline derivatives of (*S*)-citronellol were prepared and for these compounds ferroelectric (SmC^*_F) and antiferroelectric (SmC^*_A) phases were found [11]. This opens the possibility to apply these compounds in optoelectronic and display technology. It is difficult to foresee exactly liquid crystalline properties referring only to chemical structures of a molecule. So, in this paper we would like to present the synthesis and examine the thermotropic behaviour of new 4'-alkoxybiphenyl esters of trimellitimides (the IUPAC name for trimellitimide is 5-carboxy-2,3-dihydro-1*H*-isoindole-1,3-dione) with chiral tails attached to the rigid ester imide core. It should be interesting to find how the liquid crystalline properties are influenced by a structure and a position of a chiral centre in molecules. We have obtained two types of such compounds. The first group are imides with chiral substituents on the nitrogen atom. The other group are ester imides possessing the same substituents but connected to biphenyl moieties.

Imides can be easily converted into thioimides with Lawesson's reagent. The comprehensive studies of the thionation reaction mechanism have been reported many times, also in this journal [12, 13]. Now, we have applied our experience in this field to the preparation of liquid crystalline monothio- and dithioimides. We would like to compare their thermotropic properties with those of parent trimellitimides.

The synthetic pathways to the compounds studied are presented in Schemes 1 and 2.



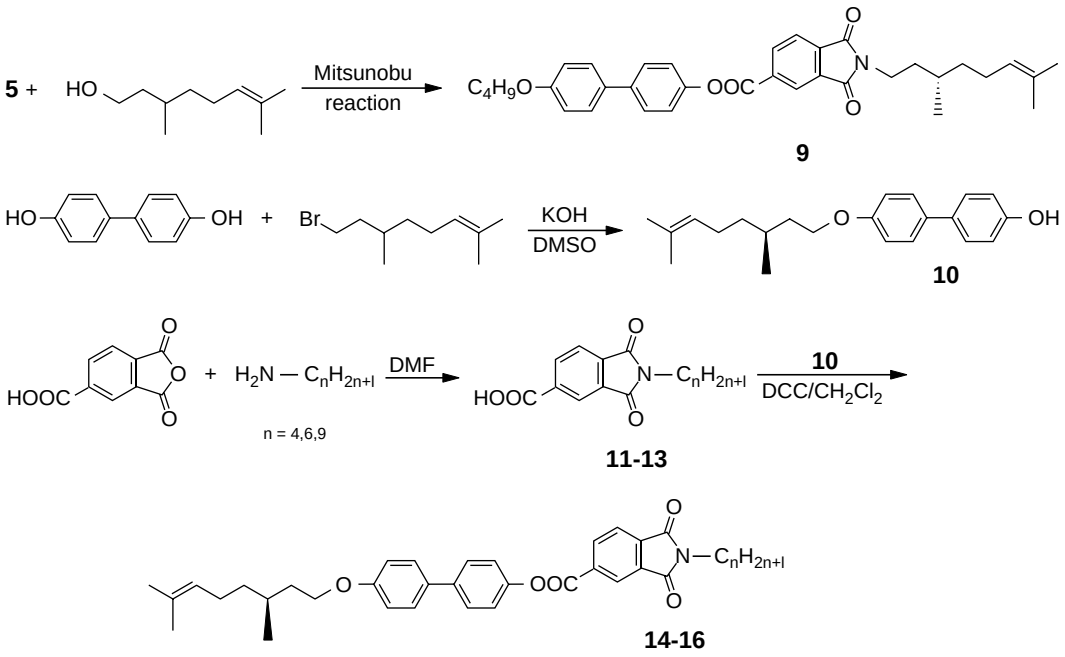
Scheme 1

Results and Discussion

The introduction of chiral tails into rod-like structures of ester imides as well as thioimides was achieved in two ways [14]. The compounds **7 - 9** having *N*-substituents with chiral centres at α- or γ-positions were derived from (*R*)-2-octanol and (*S*)-citronellol, while chirality of the imides **14-16** rests in the alkenyloxy chains attached to the biphenyl ring.

The DSC measurements revealed the presence of two or three phase transitions for all compounds occurring on heating and/or cooling courses. Also the observation by means of a polarising microscope proved that all of the imides examined exhibit liquid crystalline properties. They showed focal conic microscopic textures very typical for smectic mesophases. The miscibility with smectic C* and A phases of the well-known (*S*)-4-(2-methylbutyl)phenyl-4-octylbiphenyl-4'-carboxylate makes it possible to identify them correctly [15]. The compounds studied have SmA or both SmA and SmC* phases. The compounds **7b** and **8** exhibit monotropic transitions meaning that mesophases appear on cooling only. The temperature ranges of the mesophase are listed in Table 1.

Ester imide **7** and its sulphur analogues **7a – c** derived from 4'-butoxy-4-hydroxybiphenyl (**1**) possessing an (*S*)-*N*-2-octylimide group show only the SmA phase. The similar imide **8** with a longer aliphatic tail attached to the biphenyl moiety ($C_{11}H_{23}O$-) also exhibits a monotropic SmA phase. For the monothioimides **7a,b** and the dithioimide **7c** an introduction of sulphur atoms into carbonyl groups results in a reduction of phase transition temperatures. The compounds form only SmA phase, too. This is a consequence of a considerable change of the compound polarity and of the increase of the molecular dimensions. It should



Scheme 2

Table 1. Temperatures (°C) and enthalpies (KJ mol^{-1}) (italic characters) of phase transitions of compounds studied with DSC.

Compound	Cr_1		Cr_2		SmC*		SmA		Iso
7	–		•	143.5 *30.2*	–		•	154.8 *10.0*	•
7a	–		•	129.0 *30.7*	–		•	139.2 *8.4*	•
7b	–		•	136.2 *38.6*	–		(•	115.5 −8.8)[a]	•
7c	–		•	104.8 *28.8*	–		•	123.2 *7.9*	•
8	–		•	119.1 *46.1*	–		(•	119.0 −5.7)	•
9	–		•	113.1 *16.9*	–		•	180.2 *8.3*	•
14	–		•	103.9 *24.7*	•	122.9 *0.10*	• •	155.6 *5.7*	•
15	•	101.5 *23.6*	•	105.2 *3.0*	•	135.9 *0.23*	• *5.8*	152.1	•
16	–		• •	133.2 *38.2*	•	144.1 *0.31*	•	149.8 *6.3*	•

[a] In parentheses: monotropic transitions; • presence of mesophase.

be noticed that thioimides, in contrast to other types of thiocarbonyl compounds, are thermochemically stable. Heating them for several hours over the clearing temperature does not cause their decomposition, and temperatures of phase transitions do not alter. These results are in agreement with our previous findings [6, 10]. Also, the imide **9** with its short butoxy chain and *N*-citronellyl substituent has only a SmA mesophase. It is worth noting that its isomer, the *N*-butyltrimellitimide **14** carrying a citronellyl group on the opposite site of the molecule, shows both SmA and SmC* phases. This appears from comparing the DSC curves as well as the microscopic images of liquid crystalline textures of imides **9** and **14**. The miscibility with SmC* and SmA of the phase standard confirmed the above conclusion. The DSC curves for these isomers are shown in Fig. 2. The small thermal effect at 121 – 122 °C corresponding to a SmA-SmC* transition exists also for **14**. Fig. 3 presents the microphotographs of smectic phases of both isomers. These pictures show quite different textures of the smectic phases for the two similar compounds. So-called skew smectic phases (SmC*) occur for **15** as well as for **16**.

The results show that the presence of long chiral *N*-substituents does not warrant the appearance of a skew smectic phase (**7 – 9**). On the other hand, such aliphatic chains connected directly to the biphenyl moiety can involve SmC* phases (**14 – 16**).

It should be admitted that in our previous paper we found that for short chiral *N*-groups (2-methylbutyl- and 1-methylpropyl-), smectic C* phases were formed,

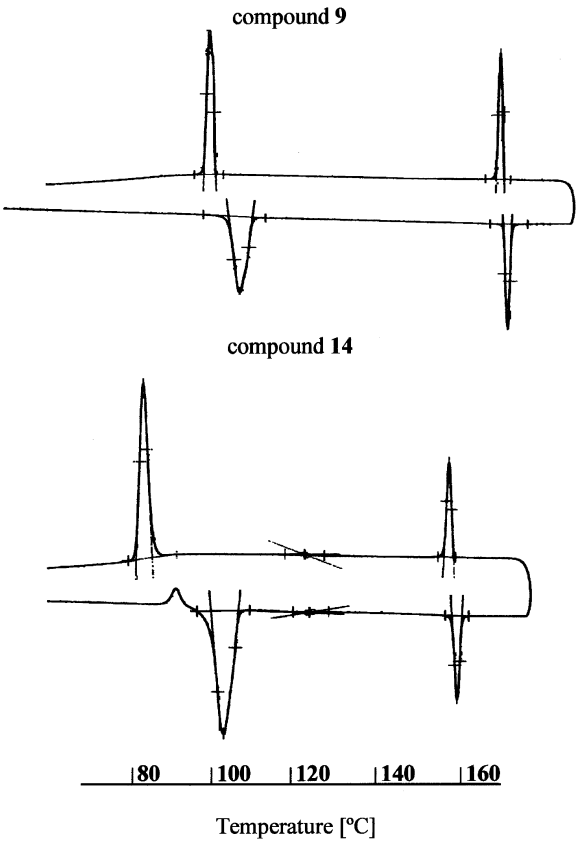


Fig. 2. Phase transitions for **9** and **14** as measured by DSC.

too. In this case, biphenyl moieties with the long undecyloxy substituent were always present [6]. The presented results as well as our former findings suggest that SmC* phases may occur on the condition that the biphenyl units contain long alkoxy tails. On the other hand, the position of a chiral centre most likely does not play the main role in the molecular ordering and for the appearance of SmA or SmC* phases.

Experimental Section

Instrumentation: All product structures were confirmed in the same way as described in the previous papers by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy [1, 5]. The infrared spectra (in CH_2Cl_2) were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrams 2000 software, and the NMR spectra (in $CDCl_3$) were recorded using a Varian Gemini 200 MHz spectrometer. The structures were confirmed also by elemental analysis and the data indicated by symbols were within $\pm$0.4% of the theoretical values. The phase transitions were observed using a polarising microscope BIOLAR equipped with a LINKAM heating stage THMs 600. Temperatures and enthalpies were measured by means of a DSC 141 SETARAM microcalorimeter. The measurements were made in both heating and cooling cycles at the rate of 1 K min^{-1}. The sample quantity was about 30 mg and special aluminium crucibles, with good thermal contact, were used. The hermetically sealed crucible with a sample was heated to the sample clearing temperature and then cooled to the crystallisation temperature. After this procedure, the DSC measurement was started. The values of temperature and enthalpy were read directly from the calorimeter integration curves after preliminary calibration using standards (gallium of 99.99% purity; 6CHBT of 99.95% purity; indium of 99.999% purity; tin of 99.999% purity). The accuracy of phase transition temperature measurements was about $\pm$0.1 K.

Synthesis: All the chemicals used were analytical grade commercial products and were applied without further purification.

4'-Butyloxy-biphenyl-4-ol (**1**) *and 4'-undecyloxybiphenyl-4-ol* (**2**): These compounds were obtained as described previously in dry DMSO on solid KOH, in room temperature; for **1**: m.p. 172 °C [16]; for **2**: m.p. 153 °C [16].

4-[(4'-Butyloxybiphenyl-4-yl)oxycarbonyl]phthalic anhydride (**3**) *and 4-[(4'-undecyloxybiphenyl-4-yl)oxycarbonyl]-phthalic anhydride* (**4**): These compounds were obtained as described previously from trimellitanhydride chloride and proper 4-alkoxybiphenols [6]. For **3**: yield 63%; m.p. 191 °C for **4** yield 58%; m.p. 174 °C. Analytical data of compound **4** were identical as described in a prior publication [6].

[(4-Butyloxybiphenyl-4'-yl)oxycarbonyl]phthalimide (**5**) *and [(4-undecyloxybiphenyl-4'-yl)oxycarbonyl]phthalimide* (**6**): The mixture of 2 mmol of **3** or **4** and 1 mmol of urea was carefully melted for 5 min. Next, the alloys were powdered and recrystallised from dry THF. For **5:** yield 77%; m. p. 239 °C; FT-IR (CH_2Cl_2): ν = 3688 (N-H), 1744 (C=O$_{imide}$), 1741 (C=O$_{ester}$), 1704 (C=O$_{imide}$) cm^{-1}. Compound **6** was identical to the one described previously; m. p. 245 °C [6].

N-[(S)-1-methylheptyl]-4-[(4'-butyloxybiphenyl-4'-yl)-oxycarbonyl]phthal-imides (**7**) *and N-[(S)-1-methylheptyl]-4-[(4-undecyloxybiphenyl-4'-yl)oxycarbonyl]-phthalimides* (**8**): The general procedure of obtaining compounds **7** and **8** according to the Mitsunobu method [6, 17] is multiply published frequently in the literature. The syntheses were carried out from equimolar amounts of (*R*)-2-octanol and imides **5** or **6**, respectively. The crude products of interest were washed with methanol, then the deposits were crystallised from heptane and next purified by means of flash-column chromatography (SiO_2) using chloroform/methanol (20:1) as an eluent.

7: Yield 20%; FT-IR (CH_2Cl_2): ν = 1777 (C=O$_{imide}$), 1741 (C=O$_{ester}$), 1716 (C=O$_{imide}$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, CH_3), 0.97 (t, 3 H,

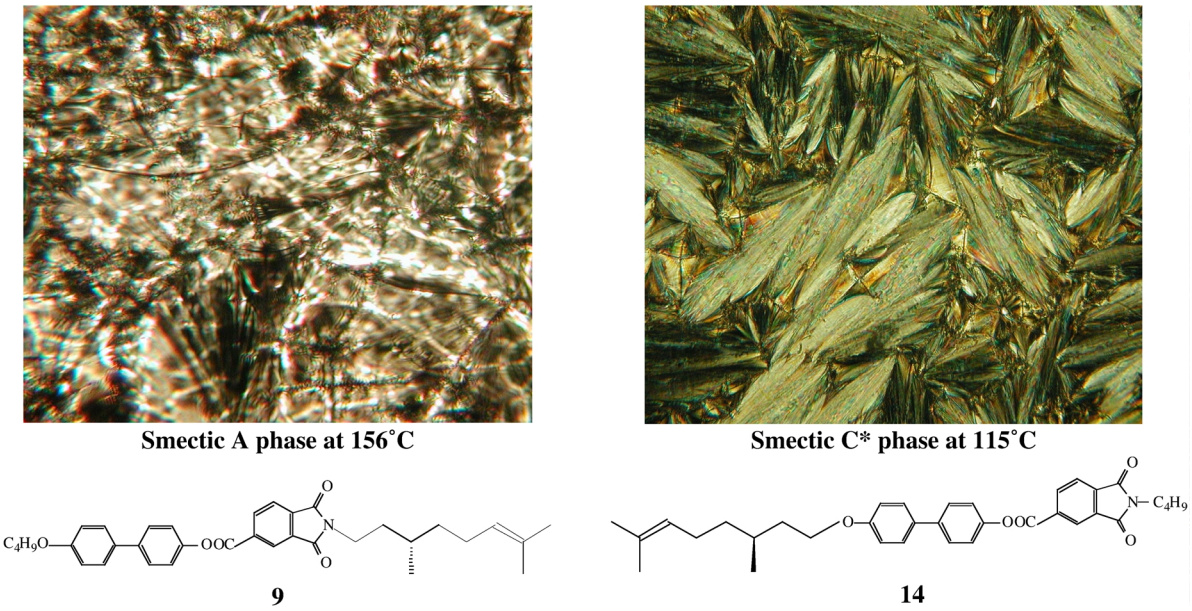


Fig. 3. Smectic textures of isomers **9** and **14**.

CH_3), 1.25 – 2.05 (m, 16 H, CH_2), 4.02 (t, 2 H, OCH_2), 4.38 (m, 1 H, NCH), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.66 (m, 4 H), 7.99 (m, 1 H_{imide}), 8.55 – 8.65 (m, 2 H_{imide}); calcd. C 75.63, H 7.93, N 2.45; found C 75.69, H 7.94, N 2.50.

8: Yield 27%; FT-IR (CH_2Cl_2): ν = 1777 ($C{=}O_{imide}$), 1740 ($C{=}O_{ester}$), 1715 ($C{=}O_{imide}$) cm^{-1} ; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, CH_3), 0.95 (t, 3 H, CH_3), 1.22,– 2.06 (m, 30 H, CH_2), 4.00 (t, 2 H, OCH_2), 4.33 (m, 1 H, NCH), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.66 (m, 4 H), 7.99 (m, 1 H_{imide}), 8.55 – 8.65 (m, 2 H_{imide}); calcd. C 77.09; H 8.88; N 2.09; found C 77.15; H 8.92; N 2.01.

Synthesis of monothioimides (**7a,b**) *and dithioimide* (**7c**): The thionation procedure by means of Lawesson's reagent was the same as described previously [6, 10, 13]. Also, the separation and identification of monothioimides, as well as of the dithioimide were performed according to the method described in detail.

7a: Yield 18%; FT-IR (CH_2Cl_2): ν = 1741 ($C{=}O_{ester0}$), 1736 ($C{=}O_{imide}$), 1277 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, CH_3), 0.97 (t, 3 H, CH_3), 1.24 – 2.07 (m, 30 H, CH_2), 4.01 (t, 2H, OCH_2), 5.03 (m, 1H, NCH), 6.96 – 7.00 (m, 2H), 7.30 (m, 2H), 7.50 – 7.66 (m, 4 H), 8.02 (m, 1 H_{imide}), 8.59 – 8.62 (m, 2 H_{imide}); calcd. C 73.56, H 7.72, N 2.38, S 5.45; found C 73.44, H 7.68, N 2.25, S 5.40.

7b: Yield 20%; FT-IR (CH_2Cl_2): ν = 1742 ($C{=}O_{ester}$), 1736 ($C{=}O_{imide}$), 1257 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, CH_3), 0.96 (t, 3 H, CH_3), 1.21 – 2.07 (m, 30 H, CH_2), 4.02 (t, 2 H, OCH_2), 5.04 (m, 1 H, NCH), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.66 (m, 4 H), 7.91 (m, 1 H_{imide}), 8.52 – 8.74 (m, 2 H_{imide}); calcd. C 73.56, H 7.72, N 2.38, S 5.45; found C 73.44, H 7.67, N 2.35, S 5.4.

7c: Yield 29%; FT-IR (CH_2Cl_2): ν = 1742 ($C{=}O_{ester}$), 1287 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.82 – 2.56 (m, 36 H), 4.02 (t, 2 H, OCH_2), 5.60 (m, 1 H, NCH), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.66 (m, 4 H), 8.04 (m, 1 H_{imide}), 8.60 – 8.65 (m, 2 H_{imide}); calcd. C 71.60, H 7.52, N 2.32, S 10.62; found C 71.45, H 7.57, N 2.35, S 10.99.

(S)-N-2-(3,7-Dimethyl-oct-6-enyl)-4-[(4-butyloxybiphenyl-4'-yl)oxy-carbonyl]phthalimide (**9**): The synthesis was the same as for the ester imides **7,8**. Compound **5** and (*S*)-citronellol were used as substrates.

Yield 29%; FT-IR (CH_2Cl_2): ν = 1776 ($C{=}O_{imide}$), 1742 ($C{=}O_{ester}$), 1736 ($C{=}O_{imide}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 – 1.03 (m, 12 H, CH_3), 1.58 – 2.06 (m, 11 H, CH_2), 3.75 (t, 2 H, OCH_2), 4.01 (t, 2 H, NCH_2), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.64 (m, 4 H), 7.99 (m, 1H_{imide}), 8.55 – 8.67 (m, 2 H_{imide}); calcd. C 76.13, H 7.77, N 2.40; found C 76.17, H 7.77, N 2.34.

4'-[(S)-3,7-Dimethyl-oct-6-enyloxy]biphenyl-4-ol (**10**): This compound was obtained as described previously from 4,4-dihydroxybiphenyl and (*S*)-citronellyl bromide [16]. M. p. 118 °C; yield 33%.

N-Alkyltrimellitimides (**11-13**): Trimellitimides with *N*-butyl, *N*-hexyl and *N*-nonyl substituents were synthesized according to the well known and patented method from trimellitic anhydride and proper amines in dry boiling DMF [18].

N-Alkyl-4-[(S)-4'-citronellylbiphenyl-4'-yl)oxycarbonyl]-phthalimide (**14-16**): The general procedure of obtaining compounds **14-16** were frequently published in the literature [6 – 10]. The synthesis was carried out from mesogenic units **10** and proper *N*-alkyltrimellitimides **11-13** in methylene chloride using dicyclohexylcarbodiimide (DCC) and DMAP as catalyst. The crude products of interest were crystallised from a benzene/methanol mixture and then the crystals were purified by means of flash-column chromatography (SiO_2) using chloroform/methanol (20:1) as an eluent.

14: Yield 28%; FT-IR (CH_2Cl_2): ν = 1776 ($C{=}O_{imide}$), 1742 ($C{=}O_{ester}$), 1736 ($C{=}O_{imide}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 – 1.08 (m, 12 H, CH_3), 1.59 – 2.06 (m, 11 H, CH_2), 3.78 (t, 2 H, OCH_2), 4.00 (t, 2 H, NCH_2), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.66 (m, 4 H), 7.99 (m, 1 H_{imide}), 8.55 – 8.67 (m, 2 H_{imide}); calcd. C 76.13, H 7.77, N 2.40; found C 76.19, H 7.76, N 2.36.

15: Yield 32%; FT-IR (CH_2Cl_2): ν = 1777 ($C{=}O_{imide}$), 1741 ($C{=}O_{ester}$), 1736 ($C{=}O_{imide}$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 – 1.03 (m, 12 H, CH_3), 1.58 – 2.06 (m, 15 H, CH_2), 3.75 (t, 2 H, OCH_2), 4.01 (t, 2 H, NCH_2), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.64 (m, 4 H), 7.99 (m, 1 H_{imide}), 8.55 – 8.67 (m, 2 H_{imide}); calcd. C 77.07, H 7.46, N 2.40; found C 77.17, H 7.49, N 2.32.

16: Yield 34%; (CH_2Cl_2): ν = 1776 ($C{=}O_{imide}$), 1741 ($C{=}O_{ester}$), 1735 ($C{=}O_{imide}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 – 1.03 (m, 12 H, CH_3), 1.56 – 2.09 (m, 21 H, CH_2), 3.75 (t, 2 H, OCH_2), 4.01 (t, 2 H, NCH_2), 6.96 – 7.00 (m, 2 H), 7.30 (m, 2 H), 7.50 – 7.64 (m, 4 H), 7.99 (m, 1 H_{imide}), 8.55 – 8.67 (m, 2 H_{imide}); calcd. C 77.15, H 8.48, N 2.14; found C 77.17, H 8.49, N 2.10.

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